



Selective reduction of NO with CO in the presence of O₂ with Ir/WO₃ catalysts: Influence of preparation variables on the catalytic performance

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ABSTRACT

Several Ir/WO₃ catalysts were prepared, which were different in the loading of Ir (up to 10 wt.%) and in the pretreatment conditions, and used for the reduction of NO (500 ppm) with CO (3000 ppm) in the presence of excess O₂ (5%), SO₂ (2 ppm), and H₂O (1%). The rate of NO conversion per unit mole of Ir was found to be maximal at a small Ir loading of 0.5–1.0 wt.%. The good catalytic performance was achieved when the Ir precursors (IrO_x) supported on WO₃ were reduced under mild conditions by He at 400 °C or H₂/He at a lower temperature of 130 °C. The catalysts were characterized by XRD, FTIR after CO adsorption, and H₂-TPR. The characterization results show that the active sites are exposed zero-valent Ir species, in accordance with previous works using Ir on WO₃ and other supports, and that the fraction of these active species is larger for a higher degree of Ir dispersion (smaller Ir particles). The preparation conditions for highly active Ir/WO₃ catalysts were confirmed and possible reaction mechanisms were discussed.

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1. Introduction

One of the important environmental issues is the removal of nitrogen oxides (NO, NO₂, and N₂O) emitted from various engines and combustors [1]. Recently, the selective catalytic reduction (SCR) of NO under oxygen-rich conditions has been attracting extensive attention for practical SCR operation, for which hydrocarbons and CO may be used as effective reducing agents [2,3]. It is reported for the SCR of NO with CO abundant in engine exhaust that Ir catalysts supported on silicate [4] and ZSM-5 [5] are active in the presence of excess O₂. Hamada et al. indicate that Ir/SiO₂ catalysts doped with various additives are active for the SCR of NO with CO in the presence of O₂ and SO₂ and larger Ir particles are more active [6–9]. Tamai et al. show the doping of Nb₂O₅ to enhance the activity of Ir/SiO₂ catalyst for the SCR of NO with CO under excess O₂ but SO₂ free conditions [10]. They attribute this enhancement to interactions of Ir with Nb₂O₅ and smaller Ir particles are easier to interact with the additive, resulting in an enhanced catalytic activity. The effectiveness of Ir on Ce-doped γ-Al₂O₃ is reported for the SCR of NO with CO in the presence of O₂ at a higher temperature of 700 °C by Iliopoulou et al. [11]. The present authors screened various Ir catalysts using different support materials and showed Ir/WO₃ to be one of promising catalysts [12–

14]. This catalyst is highly active even in the presence of excess O₂ or O₂ + SO₂, which is beneficial for sulfur-free lean-burn engines. The influence and optimization of preparation variables should be further studied for more effective use of supported Ir catalysts under practical conditions.

Following previous works [12–14], the present work has been undertaken to improve the performance of Ir/WO₃ catalysts for the SCR of NO with CO in the presence of excess O₂, SO₂, and H₂O under reaction conditions similar to practical operating conditions. For this purpose, the effects of such preparation variables as metal loading and pretreatment conditions on their activities were investigated in detail. The catalytically active sites were elucidated by different characterization methods including XRD, FTIR, TPR, and TEM, and the conditions for the preparation of active sites, zero-valent Ir sites exposed on smaller Ir particles, were confirmed. It has been shown that smaller metal loading (smaller metal particles) and reduction of supported Ir precursors under mild conditions are required to prepare active Ir/WO₃ catalysts. In addition, possible reaction mechanisms are also discussed, in particular on the contribution of NO decomposition to the SCR of NO with CO over Ir/WO₃ catalysts.

2. Experimental

The experimental procedures used in this work are similar to those used previously [14–16]. So, these will be described in brief in the following.

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Table 1

Various oxide materials used as supports for Ir catalysts

Support	Surface area ^a (m ² g ⁻¹)	Source/preparation
WO ₃	24	Thermal decomposition of H ₂ WO ₄ (Aldrich) at 400 °C for 3 h
SiO ₂	243	Fuji Silysia (Calyact 10)
γ-Al ₂ O ₃	155	CSJ ^b (ALO8)
ZnO	26	Thermal decomposition of ZnCO ₃ (Wako) at 500 °C for 3 h
Ta ₂ O ₅	6	Wako
Sb ₂ O ₅	47	Junsei
Nb ₂ O ₅	15	Kishida
CeO ₂	15	Wako
MoO ₃	7	Wako

^a BET surface area.^b Catalysis Society of Japan.

2.1. Catalyst preparation

Various support materials were used to prepare supported Ir catalysts. Table 1 lists the kinds of oxide supports used and their sources and BET surface areas measured by nitrogen adsorption. An impregnation method was used to prepare supported Ir catalysts [12,14]. The support was impregnated with H₂IrCl₆ aqueous solution and the solvent was removed by evaporation in a rotary evaporator at 70 °C and under reduced pressure. The sample so obtained was screened, the particulates of 24–60 mesh in size were collected, and these were calcined in air at 400 °C for 3 h. The catalyst samples were treated in a He stream at 400 °C for 1 h, otherwise unnoticed, prior to reaction and TPR runs. For Ir/WO₃, the metal loading, Ir/(Ir + WO₃), was changed up to 10 wt.%.

2.2. NO reduction with CO

The reaction runs were carried out in a conventional flow reactor made of 6–9 mm diameter Pyrex glass tubing in which a catalyst sample of 0.05 g was mounted on loosely packed quartz wool. The gaseous mixture of NO 500 ppm, CO 3000 ppm, O₂ 5%, SO₂ 2 ppm, and H₂O 1% diluted with He was passed through the catalyst bed at 50 cm³ min⁻¹. The concentrations of exiting gaseous components were determined by gas chromatographs (Shimadzu 8A and 6A) with porapak Q and molecular sieve 5A columns and that of NO₂ was monitored using a UV–vis spectrophotometer (Hitachi U-1100).

2.3. Catalyst characterization

A Fourier transform-infrared spectroscopy (JASCO FTIR-620) with a diffuse reflectance attachment (DG-500/H) was used to examine the state of exposed Ir species of Ir/WO₃ catalysts [17,18]. After CO was adsorbed on a catalyst sample by passing a stream of

10 cm³ min⁻¹ at room temperature for 30 min, the sample was subjected to the FTIR measurement under ambient conditions. The FTIR spectra collected were used to differentiate exposed Ir⁰ and Ir^{δ+} species. Temperature-programmed reduction was performed to examine the reduction behavior of various Ir/WO₃ samples different in metal loading and pretreatment conditions. A sample (0.5 g) was heated at a rate of 5 K min⁻¹ while passing a stream of H₂ (5% in N₂) at 50 cm³ min⁻¹. The amount of H₂ consumed was measured by TCD as a function of temperature. The structural features of catalyst samples prepared were characterized by XRD (JEOL JDX-8200) and TEM (JEOL JEM-2010F) measurements.

3. Results and discussion

3.1. Screening of various supported Ir catalysts

Previously, the authors screened various supported Ir catalysts for NO (1000 ppm) reduction with CO (1%) in the presence of O₂ (2%) and showed Ir/WO₃ and Ir/ZnO to be active catalysts [12]. For practical application, however, the catalysts should also be active under O₂ richer conditions similar to practical ones. So, similar screening has also been made at a higher O₂ concentration of 5% for CO 3000 ppm in the presence of SO₂ (2 ppm) and H₂O (1%) as well. Table 2 summarizes the results of NO reduction with CO at temperatures of 200–400 °C for 5 wt.% Ir catalysts using various support materials. The oxide supports in which the metals are in the high oxidation number (as in WO₃ and Nb₂O₅) were used. The Ir/WO₃ catalyst was again observed to be the most active and indicate a high total conversion of NO to N₂ and N₂O of 28.8% at 300 °C with a high selectivity to N₂ of 88%. The Ir/Nb₂O₅ and Ir/Ta₂O₅ were also active, which showed good conversion levels of 25% and 16.4%, respectively, at 325 °C. The Ir/SiO₂ catalyst was more active at low temperatures compared with the other ones but, unfortunately, the selectivity to the undesired product of N₂O was higher, being 76% at 250 °C, for example. Those results demonstrate that the Ir/WO₃ catalyst is most effective under O₂ richer conditions. Then, preparation variables were optimized to improve the activity of this catalyst.

3.2. Optimization of metal loading for Ir/WO₃

The Ir loading was changed in the range of up to 10 wt.%. Fig. 1 shows the results of NO and CO conversion for several Ir/WO₃ catalysts at temperatures of 200–400 °C. The support itself is inactive and the activities of the supported Ir catalysts change similarly with temperature. Either NO conversion or CO conversion increases with the loading of Ir up to 5 wt.%; however, the 10 wt.% Ir/WO₃ catalyst is less active for the conversion of NO and CO. For these runs, the same amounts of the catalyst samples were used and so the amounts of Ir used were different. Fig. 2 gives the rate of

Table 2

Activities of various 5 wt.% Ir supported catalysts using different support materials for the reduction of NO with CO

Support	NO conversion to N ₂ (N ₂ O) (%)						CO conversion to CO ₂ (%)					
	225 °C	250 °C	275 °C	300 °C	325 °C	350 °C	225 °C	250 °C	275 °C	300 °C	325 °C	350 °C
WO ₃	3.9(0)	6.1(5.0)	13(6.2)	25(3.8)	17(0)	13(0)	12	24	85	96	100	100
SiO ₂	3.2(0)	5.5(12)	4.1(13)	2.8(8.3)	2.6(0)	1.2(0)	4.7	38	92	100	100	100
Al ₂ O ₃	0(0)	1.1(0)	1.9(0)	2.9(0)	3.5(0)	1(0)	1.4	8.9	21	49	84	99
ZnO	1.4(0)	4.8(0)	3.9(7.1)	4.1(2.4)	4.1(0)	4.6(0)	16	26	79	91	95	98
Ta ₂ O ₅	0(0)	0(0)	4.9(4.0)	8.8(6.7)	14(2.4)	9.0(0)	3.2	8.2	37	100	100	100
Sb ₂ O ₅	0(0)	1.1(0)	1.4(0)	1.5(0)	2.3(0)	0(0)	7.2	18	53	100	100	100
Nb ₂ O ₅	0(0)	0.9(0)	7.6(6.0)	13(3.8)	25(0)	10(0)	12	24	99	100	100	100
CeO ₂	1.3(0)	1.9(0)	5.5(2.9)	6.6(0)	9.3(0)	4.4(0)	11	18	59	100	100	100
MoO ₃	0.5(0)	1.8(0)	1.7(0)	3.7(9.1)	2.3(7.2)	1.8(4.3)	19	48	87	98	100	100

Reaction conditions: NO 500 ppm; CO 3000 ppm; O₂ 5%; SO₂ 2 ppm; H₂O 1% (in He). Pretreatment: He, 400 °C, 1 h.

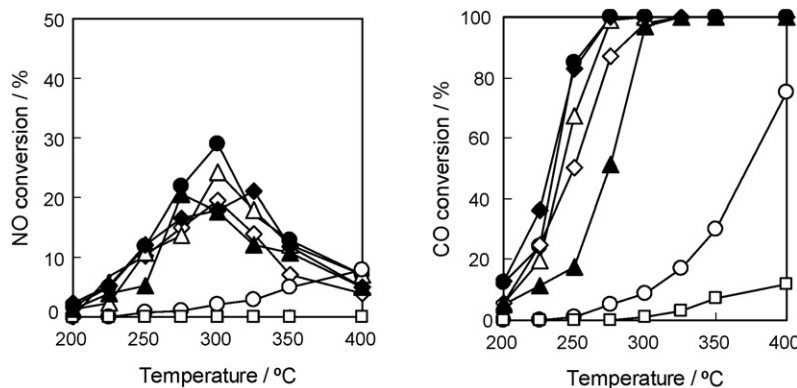


Fig. 1. Results of NO reduction with CO in the presence of O_2 using Ir/WO_3 catalysts different in the metal loading. Ir wt.-%: 10 (Δ), 5 (\bullet), 3 (\blacklozenge), 1 (\diamond), 0.5 (\blacktriangle), 0.1 (\circ), 0 (\square). Pretreatment: He, 400 °C, 1 h. Reaction conditions: NO 500 ppm, CO 3000 ppm, O_2 5%, SO_2 2 ppm, H_2O 1% (in He).

NO reduction per unit mole of Ir against the metal loading at 225 °C and 250 °C. The results indicate that the rate is maximal at a smaller Ir loading of 0.5–1.0 wt.%, at which the Ir species can function most effectively.

Fig. 3 gives the selectivity for the NO conversion to N_2 against the total NO conversion. The relation of N_2 selectivity against NO conversion may be roughly correlated with a single line for the data at each reaction temperature, except for the 0.5 wt.-% Ir/WO_3 catalyst for which the CO conversion is high (>50%) but a small amount of CO remains un-reacted. So, we suggest that the catalytic natures of the Ir/WO_3 catalysts for the reduction of NO with CO do not change so much with the Ir loading.

Fig. 2 suggests that physical/chemical properties of supported Ir species may change significantly with the metal loading. Previously the authors reported that the metallic, zero-valent Ir species were active sites for the reduction of NO with CO [14]. For the catalyst samples different in the metal loading, the surface of supported Ir species was examined by FTIR measurements at room temperature following CO adsorption. Fig. 4 shows FTIR spectra collected with the three samples after the NO reduction at 250 °C. The assignment of the absorption bands observed was made according to the literature [7,8,17,18]. An absorption peak is seen at 2073 cm^{-1} , assignable to Ir^0-CO , for the 1 wt.-% Ir sample, in which the Ir species exist chiefly in the zero-valent state. For 5 wt.-% sample, an additional absorption is also observed with the peak

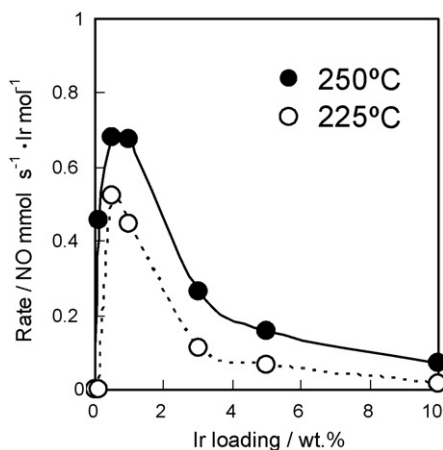


Fig. 2. Rate of NO reduction per unit mole of Ir for Ir/WO_3 catalysts different in the metal loading at reaction temperatures of 250 °C and 225 °C. Pretreatment: He, 400 °C, 1 h. Reaction conditions: NO 500 ppm, CO 3000 ppm, O_2 5%, SO_2 2 ppm, H_2O 1% (in He). The rate of NO reduction was calculated by (rate of NO flow into reactor in mmol/s) (total conversion of NO)/(mass of Ir in catalyst used in mol).

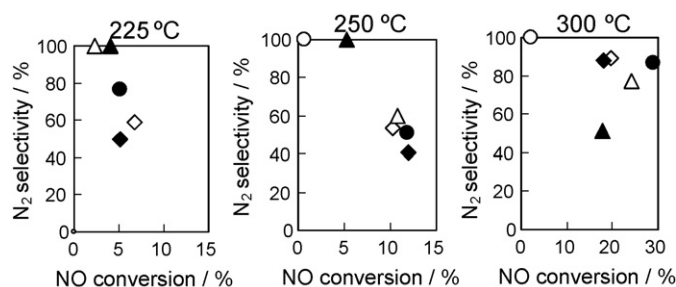


Fig. 3. Plots of N_2 selectivity against total NO conversion in the reduction of NO with CO at reaction temperatures of 225 °C, 250 °C, and 300 °C for Ir/WO_3 catalysts different in the metal loading. Ir wt.-%: 10 (Δ), 5 (\bullet), 3 (\blacklozenge), 1 (\diamond), 0.5 (\blacktriangle), 0.1 (\circ). Pretreatment: He, 400 °C, 1 h. Reaction conditions: NO 500 ppm, CO 3000 ppm, O_2 5%, SO_2 2 ppm, H_2O 1% (in He). At 225 °C, the catalyst was inactive and the selectivity was unable to be determined; thus, five data are plotted herein.

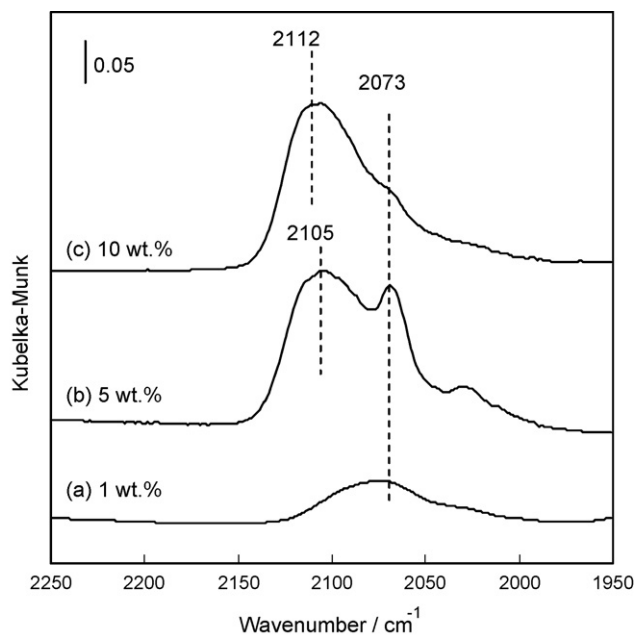


Fig. 4. FTIR spectra for 1 wt.%, 5 wt.%, and 10 wt.-% Ir/WO_3 catalysts after the NO reduction with CO at 250 °C followed by CO adsorption. Pretreatment: He, 400 °C, 1 h. Reaction conditions: NO 500 ppm, CO 3000 ppm, O_2 5%, SO_2 2 ppm, H_2O 1% (in He).

located at about 2100 cm^{-1} , which is assigned to $\text{Ir}^{\delta+}\text{-CO}$. When the Ir loading is increased to 10 wt.%, this absorption band becomes larger compared with that at 2073 cm^{-1} . Those results demonstrate that the fraction of exposed Ir^0 species significantly depends on the Ir loading; the Ir species are in the zero-valent state for the 1 wt.% sample, while in the partially oxidized state for the 10 wt.% one. Both zero-valent and partially oxidized Ir species exist on the surface of the 5 wt.% sample but a larger fraction of Ir species should be in the partially oxidized state. This change of the state of exposed Ir species with the metal loading may explain the results of Fig. 2.

We tried to measure the size of supported Ir particles for the catalyst samples different in the Ir loading by using XRD and TEM. The size was not possible to estimate by XRD since the particle size should be smaller than the limit of detection and the 2θ values are close to those of the support WO_3 . Unfortunately, it was also difficult to differentiate Ir particles due to similarity of the density to electron beam between Ir and WO_3 . We may assume, however, that the size of supported Ir particles is smaller for a smaller Ir loading on WO_3 support. It is thus suggested from the above-mentioned results that the smaller metal particles expose a larger fraction of catalytically active, zero-valent Ir species on their surface. Previously Haneda et al. reported for the NO reduction with CO with Ir/SiO_2 catalysts that larger Ir particles were more active and that this was because the larger metal particles were more difficult to be oxidized under reaction conditions [8]. For inert support materials like SiO_2 , smaller metal particles should be easier to vary their properties (via oxidation/reduction of Ir particles) by contact with reactive species included in reaction mixture. However, Tamai et al., who used Nb_2O_5 doped Ir/SiO_2 catalysts, reported that smaller Ir particles interacted more strongly with the additive and this improved the resistance of Ir species to oxidation [10]. For our Ir/WO_3 catalysts, it is also suggested that the support plays a role through metal-support interactions in allowing smaller metal particles to expose active zero-valent Ir species under the reaction conditions used.

The features of Ir/WO_3 samples different in the metal loading were further examined by TPR. Fig. 5 gives the TPR patterns obtained with the three different samples. For Ir 1 wt.% sample, H_2 was consumed at temperatures up to 80°C and at temperatures above 350°C . The former is ascribed to the reduction of IrO_x species and the latter to that of the support WO_3 . The amount of H_2 consumed at temperatures below 100°C indicates the almost complete reduction of IrO_2 to Ir and that at temperatures above 330°C the reduction of WO_3 to $\text{WO}_{2.9}$. The latter reduction is also confirmed by XRD (Fig. 6).

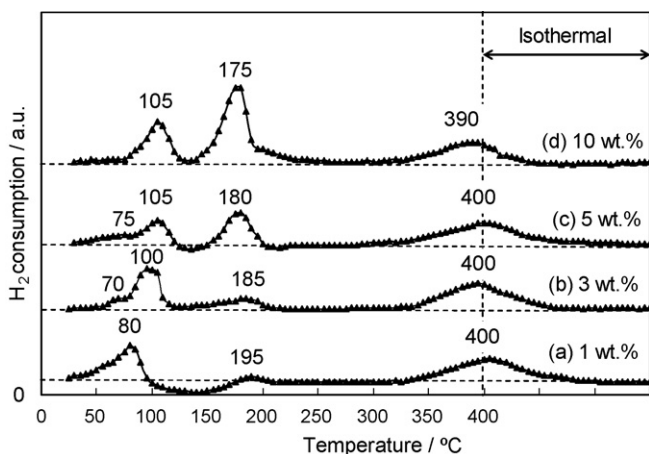


Fig. 5. TPR profiles for Ir/WO_3 catalysts different in the metal loading of 1–10 wt.%. Pretreatment: He, 400°C , 1 h.

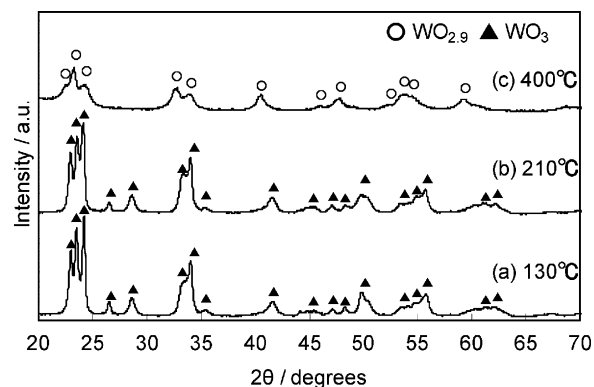


Fig. 6. XRD pattern for 5 wt.% Ir/WO_3 catalysts collected after TPR at temperatures up to 130°C , 210°C , and 400°C .

The negative consumption at $100\text{--}180^\circ\text{C}$ of TPR may be due to desorption of H_2 that is adsorbed on the surface of previously reduced Ir species at lower temperatures. When the Ir loading is increased to 5 wt.%, the reduction of IrO_x species occurs at higher temperatures and indicate two H_2 consumption peaks at 105°C and 180°C . Similar but larger consumption peaks are seen for 10 wt.% sample and the high temperature peak becomes stronger. The amounts of H_2 consumed at 330°C or above are similar for these three samples. The TPR results show that the IrO_x species can be more easily reduced for a smaller Ir loading of 1 wt.%, which is in line with the above-mentioned finding that a major fraction of exposed Ir species is in the zero-valent state for such a small Ir loading (Fig. 4). Fig. 5 shows the existence of two peaks for the reduction of IrO_x species at temperatures below 200°C . The reduction peak at around 180°C increases with the metal loading, and so the two reduction peaks might be explained by difference in the size of dispersed Ir precursors; when the metal loading is increased, the larger Ir precursors are formed and these are more difficult to be reduced compared with the smaller ones. The low- and high-temperature reduction peaks might correspond to smaller and larger Ir precursors, respectively. The support, WO_3 , could influence the reduction behavior of small and large IrO_x precursors in different manners. If so, however, the separation of the two peaks is too clear-cut. At present, unfortunately, the authors cannot make a further detailed discussion.

The FTIR measurements with CO were made to examine the surface of supported Ir particles after reduction up to different temperatures of TPR. Fig. 7 shows the FTIR spectra for 5 wt.% Ir/WO_3 sample and an absorption band ascribable to $\text{Ir}^0\text{-CO}$ appears after the reduction up to 130°C . Absorption band is little seen for this sample reduced at high temperatures of 210°C and 400°C . The high temperature reduction is likely to cause metal sintering and decrease the quantity of exposed Ir species and then that of CO adsorbed, giving no appreciable absorption band. On reduction at 400°C , however, the Ir particles did not grow beyond the size detectable by XRD (Fig. 6).

The above-mentioned results indicate that the amount of zero-valent Ir species is an important factor determining the activity of Ir/WO_3 catalyst and it depends on the metal loading, which may modify the reduction/oxidation behavior of supported Ir species during catalyst preparation. Hence, pretreatment conditions were regulated to improve the catalytic performance for the reduction of NO with CO in the presence of excess O_2 .

3.3. Improvement of activity for Ir/WO_3

Table 3 shows the catalytic activities of 5 wt.% Ir/WO_3 samples pretreated with He and/or H_2 at 130°C or 400°C . The sample

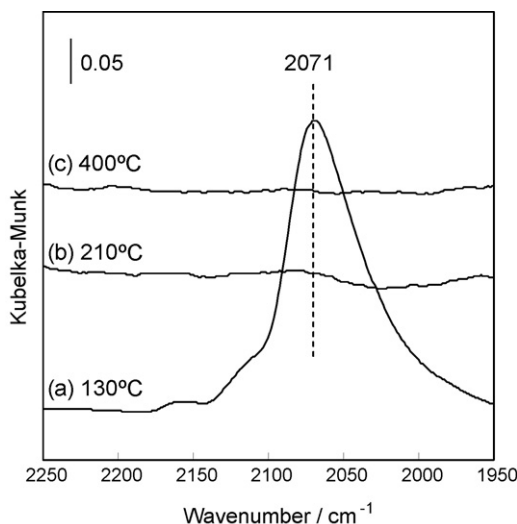


Fig. 7. FTIR spectra for 5 wt.% Ir/WO₃ catalysts collected after TPR at temperatures up to 130 °C, 210 °C, and 400 °C followed by CO adsorption.

treated (reduced) with He alone at 400 °C shows a total NO conversion of 32.2% with a high N₂ selectivity of 87%. The reduction with H₂/He at 130 °C enhances the total conversion up to 53.1% but the N₂ selectivity is a little decreased to 78%. The NO conversion is decreased to 20.1% after the reduction at a higher temperature of 400 °C, which gives a smaller N₂ selectivity of 30.8%. The surface of supported Ir species after the reaction runs was examined by FTIR with CO. Fig. 8 shows that the catalyst reduced at 130 °C has an absorption band assignable to Ir⁰–CO; however, the one reduced at 400 °C has no absorption band while the catalyst treated with He alone shows two absorption bands of Ir⁰–CO and Ir³⁺–CO species. Fig. 9 gives the XRD patterns collected after the reaction runs. The support is in the form of WO₃ and no other oxides (like WO_{2.9}) are detectable for all the catalysts, irrespective of the pretreatments used. For the sample reduced with H₂ at 400 °C, we may see a marginal XRD signal indicating the presence of Ir metal. Thus, the surface of metal particles exposes Ir species in the state of Ir⁰ and Ir^{δ+} for the sample treated with He; the treatment with He causes a partial reduction of IrO_x species. The reduction with H₂/He at a mild temperature of 130 °C completes the reduction to zero-valent Ir from IrO_x but does not cause a significant metal sintering. The metal sintering should occur on the reduction at 400 °C although the reduction to Ir is completed.

The present results indicate that zero-valent Ir species are active sites for the reduction of NO with CO over Ir/WO₃ catalysts, in accordance with the previous works [8,10,14]. It is important that Ir precursors (IrO_x) should be highly dispersed on the surface

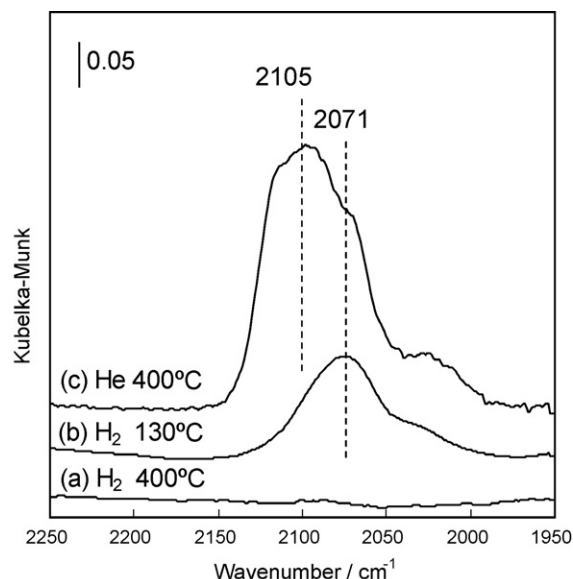


Fig. 8. FTIR spectra for 5 wt.% Ir/WO₃ catalysts pretreated in different ways and used for the reduction of NO at 300 °C followed by CO adsorption.

of WO₃ support to take a higher catalytic activity. The high dispersion of Ir precursors will lead to a high degree of Ir dispersion after reduction, which gives a larger amount of exposed Ir species. In addition, the highly dispersed Ir precursors on WO₃ are easier to reduce, resulting in a larger fraction of catalytically active Ir⁰ species exposed on a smaller Ir particle.

3.4. Consideration of reaction mechanisms on Ir/WO₃

The authors recently proposed reaction mechanisms for the reduction of NO with CO over Ir/WO₃ catalysts in the presence of O₂ [14]. Previous FTIR results indicate that OC–Ir–NO and Ir–NO species exist on the surface at low O₂ concentrations and also Ir–NO₂ at high O₂ concentrations. In addition, we assume the existence of such adsorbed species as Ir–N, Ir–O, and Ir–CO. The interactions of those adsorbed species with the other adsorbed and/or gaseous species (NO, CO) contribute to the reduction of NO to N₂ and N₂O (Scheme 1 in [14]). The Ir–N species are assumed to form by the removal of CO₂ from a single species of OC–Ir–NO and from such a pair of species as Ir–NO and Ir–CO. The previous reaction mechanisms may also apply for the present NO reduction with CO under similar reaction conditions. The mechanisms did not consider the decomposition of NO leaving Ir–N and Ir–O species. Recently Takahashi et al. pointed out the importance of NO

Table 3

Influence of pretreatment conditions on the activity of 5 wt.% Ir/WO₃ catalyst for the reduction of NO with CO at 300 °C^a

Pretreatment	NO conversion to		CO conversion to CO ₂
	N ₂	N ₂ O	
He, 400 °C, 1 h	28.1%	4.1%	100%
H ₂ /He ^b , 130 °C, 1 h	41.4%	11.7%	100%
H ₂ /He ^b , 400 °C, 1 h	6.2%	13.9%	100%

^a Reaction conditions: in a time on stream of 2 h. See footnote of Table 2 for other conditions.

^b H₂ = 5%.

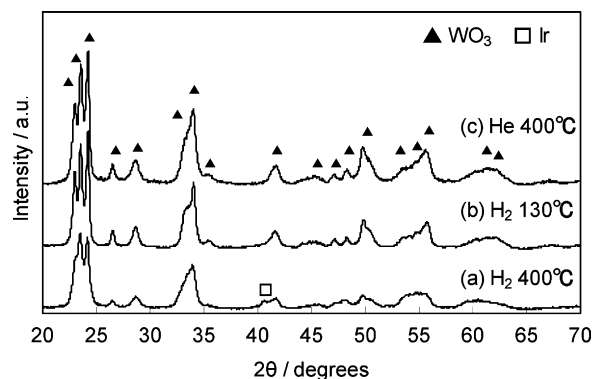


Fig. 9. XRD patterns of 5 wt.% Ir/WO₃ catalysts pretreated in different ways and used for the reduction of NO with CO at 300 °C.

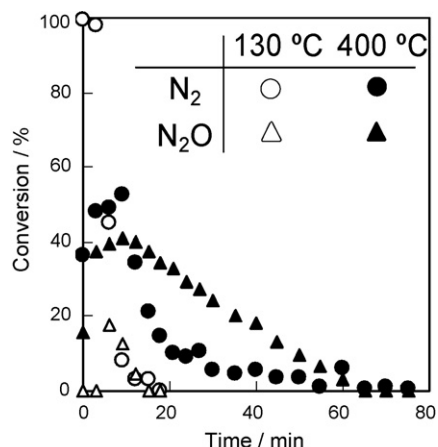


Fig. 10. Results of NO decomposition to N_2 and N_2O at 300 °C over 5 wt.% Ir/ WO_3 catalysts pretreated in 5% H_2/He at 130 °C and 400 °C for 1 h.

decomposition in the reduction of NO with CO over Ir/ SiO_2 and Ir/ WO_3-SiO_2 catalysts at 300 °C [19]. According to their pulse reactions, the formation of N_2 was observed for the first pulse only for the former catalyst while it was observed for several pulses for the latter one but the amount of N_2 formed became leveled off to a negligible level. But the authors assumed the dissociation of a NO molecule forming adsorbed N and O species followed by reactions of adsorbed O and CO species and of two adsorbed N species, giving CO_2 and N_2 gases, respectively. Thus, we have also examined the decomposition of NO with our Ir/ WO_3 catalysts and its possibility and contribution to the reduction of NO with CO will be discussed hereinafter.

The decomposition of NO was examined by passing a stream of NO (500 ppm in He) at $50\text{ cm}^3\text{ min}^{-1}$ over 5 wt.% Ir/ WO_3 catalyst samples. No decomposition was observed to occur for the catalyst that was pretreated with He at 400 °C. However, the decomposition of NO occurred on the catalysts that were reduced by H_2/He at 130 °C and 400 °C. Fig. 10 shows the conversion of NO to N_2 and N_2O as a function of time on stream. For the former sample, the complete decomposition occurs initially but stops in a short period of time of 20 min. The total amount of O that may remain on the catalyst during the decomposition of NO to N_2 is estimated to be $134\text{ }\mu\text{mol g}_{\text{catal}}^{-1}$, which is smaller than that ($268\text{ }\mu\text{mol g}_{\text{catal}}^{-1}$) of H_2 consumed to reduce IrO_2 to Ir during TPR up to 130 °C (Fig. 5). Then, all the Ir species cannot be oxidized with O produced by the NO decomposition. The FTIR after CO adsorption (not shown) indicates that an absorption band appears at 2076 cm^{-1} , assignable to Ir^0-CO , for this catalyst after the NO decomposition. Therefore, the exposed Ir species still exist in the zero-valent state after the NO decomposition and the O species formed during the initial period of NO decomposition should be mainly adsorbed on the support. The catalyst reduced at 400 °C is more active and the decomposition of NO continues for a longer time but it also stops in 75 min, which gives a quantity of O formed of $334\text{ }\mu\text{mol g}_{\text{catal}}^{-1}$, 2.5 times larger than the above-mentioned sample reduced at 130 °C. This O quantity is roughly similar to the quantity of O necessary to oxidize the support from $WO_{2.9}$ to WO_3 , $410\text{ }\mu\text{mol g}_{\text{catal}}^{-1}$; so, the O species may be used to oxidize the support, which is confirmed by XRD measurements (Fig. 11). Sica and Gigola studied NO decomposition over a Pd- WO_x/Al_2O_3 catalyst at 400 °C [20] and observed a rapid deactivation similar to the results of Fig. 10. The O species formed during the decomposition of NO may be also used to oxidize the support to WO_3 . The present results of

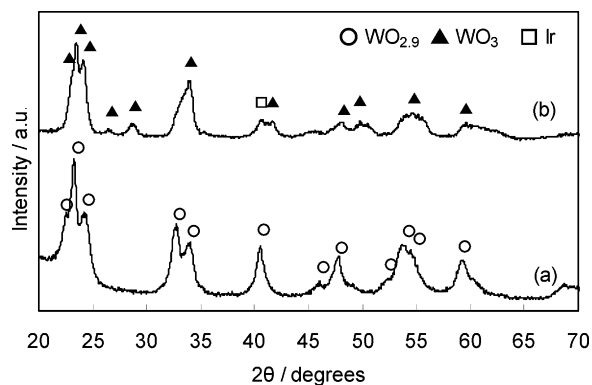


Fig. 11. XRD patterns of 5 wt.% Ir/ WO_3 catalysts pretreated in 5% H_2/He at 400 °C before (a) and after (b) the NO decomposition to N_2 and N_2O at 300 °C.

reaction runs with pure NO suggest a possibility of NO decomposition on Ir/ WO_3 catalysts under the conditions used for the reduction of NO with CO in the presence of O_2 , SO_2 , and H_2O . We believe, however, that the contribution of NO decomposition is less significant because it should stop in an early stage of reaction and the O species formed should not affect the nature of exposed Ir species.

The authors think that the active species of Ir/ WO_3 catalysts are zero-valent Ir sites exposed on the surface of supported Ir particles. The quantity of these active sites depends on the size of Ir particles and the chemical state of their surfaces, which should both change with the metal loading and the reduction (pretreatment) conditions. Small particles of supported Ir precursors are easy to be reduced (from TPR and FTIR) and higher dispersion of Ir precursors should result in higher dispersion of reduced Ir metal. When the metal loading is increased but the size of dispersed Ir precursors does not change, the quantity of exposed active Ir species is proportional to the metal loading and the specific rate of NO reduction per unit mass of Ir species should be the same, as in the cases of 0.5 and 1.0 wt.% Ir samples of Fig. 2. When the reduction is still easy but the size of dispersed Ir precursors increases (producing larger Ir particles), the specific rate should decrease with the metal loading. When the size of Ir precursors is larger and their reduction becomes difficult, the specific rate should further decrease. This may be the case for the samples of metal loadings $\geq 1\text{ wt.}\%$ of Fig. 2. An exception is the sample of the smallest metal loading of 0.1 wt.%. The state of dispersed Ir precursors might be different from that of the other samples of larger metal loadings.

As above-mentioned, when the Ir precursors are more highly dispersed on the surface of WO_3 support, it is easier to reduce them and make more zero-valent Ir sites exposed under mild reduction conditions that will cause no metal sintering. Haneda et al. showed that larger Ir particles on an inert support of SiO_2 were more difficult to be oxidized and could expose more reduced Ir sites active for the reduction of NO with CO in the presence of O_2 [8]. For Nb_2O_5 -modified Ir/ SiO_2 catalysts, however, Tamai et al. reported that smaller Ir particles could have strong interactions with Nb_2O_5 and this made supported Ir species stronger against oxidation [10]. Regalbuto and Wolf studied the NO-CO reaction with Pt/ SiO_2 catalyst modified by addition of WO_3 [21]. They showed that the WO_3 -modified Pt/ SiO_2 catalyst was more active compared with Pt/ SiO_2 and they ascribed this promotional effect to the creation of active Pt- WO_x sites resulting from the decoration effect of WO_x moieties on the surface of Pt particles. For the present Ir/ WO_3 catalysts, the support should influence the reduction behavior of Ir

species dispersed on its surface but further study is needed for detailed physical/chemical explanation.

4. Conclusion

The present results demonstrate that Ir/WO₃ is the most active catalyst for the reduction of NO with CO in the presence of excess O₂ (with SO₂ and H₂O) compared with other Ir catalysts supported on SiO₂, γ -Al₂O₃, ZnO, Ta₂O₅, Sb₂O₅, Nb₂O₅, CeO₂, and MoO₃. The catalytic performance of Ir/WO₃ catalysts depends on Ir loading and pretreatment conditions. The rate of NO conversion per unit mole of Ir shows a maximum at a small Ir loading of 0.5–1.0 wt.%. The higher catalytic activities can be achieved when the Ir precursors (IrO_x) supported on WO₃ are reduced under mild conditions by He at 400 °C or H₂/He at a lower temperature of 130 °C. The catalysts were characterized by XRD, FTIR after CO adsorption, and H₂-TPR. These characterization results show that the catalytically active sites are exposed zero-valent Ir species and the fraction of these species is larger for a higher degree of Ir dispersion (smaller Ir particles). It was observed that the decomposition of pure NO occurred on the Ir/WO₃ catalysts reduced by H₂/He but the catalysts immediately deactivated. The contribution of NO decomposition is believed to be less significant for the reduction of NO with CO over Ir/WO₃ catalysts under the present conditions.

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